

Deep desulfurization of gasoline by selective adsorption over solid adsorbents and impact of analytical methods on ppm-level sulfur quantification for fuel cell applications

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Abstract

The objectives of this work were to comparatively study the performance of a Ni-based adsorbent and a Cu(I)Y-zeolite for the desulfurization of a commercial gasoline by fixed-bed adsorption experiments at room temperature and 200 °C, and to clarify the impacts of analytical methods on the ppm-level sulfur quantification in desulfurized liquid fuels for fuel cell applications. A series of standard fuel samples containing known amounts of sulfur compounds in *n*-decane was prepared and was analyzed by using gas chromatograph coupled with a flame photometric detector (GC-FPD), pulsed flame photometric detector (GC-PFPD) and a total sulfur analyzer. The results show that the GC-FPD and GC-PFPD are not suitable for quantitative estimation of total sulfur concentration in complex hydrocarbon fuels at low ppm-level without considering both the nonlinear response and the quenching effect. The adsorptive desulfurization of a commercial gasoline over the Cu(I)Y-zeolite and a Ni-based adsorbent was conducted and compared using a fixed-bed adsorption system. The Cu(I)Y-zeolite prepared in the present study showed a breakthrough capacity of 0.22 mg S/g of adsorbent (mg/g) at room temperature for removing sulfur in a commercial gasoline to less than 1 ppmw. Under the same experimental conditions, the Ni-based adsorbent exhibited a breakthrough capacity of 0.37 mg/g. The breakthrough capacity of the Ni-based adsorbent was increased by 38% at 200 °C. Moreover, the breakthrough capacity of the Ni-based adsorbent corresponding to the outlet sulfur level of 10 ppmw was 7.3 mg/g, which was over an order of magnitude higher than that of Cu(I)Y-zeolite.

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1. Introduction

Ultra-deep removal of sulfur from transportation fuels, particularly from gasoline and diesel, has become very important in petroleum refining industry worldwide not only due to the heightened interest for cleaner air and thus increasingly stringent environmental regulations for fuel sulfur concentration, but also because of the great importance for making ultra-low-sulfur fuels for fuel cell applications [1–3]. Owing to their higher energy density and readily existing infrastructure for production, delivery and

storage, liquid hydrocarbon fuels such as gasoline are considered to be the promising primary fuels for automotive and portable fuel cells, especially for the proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) [3]. However, the current commercial fuels such as gasoline contain significant amounts of sulfur, up to 350 parts per million by weight of sulfur (ppmw) [1]. The sulfur compounds in gasoline and H₂S produced from these sulfur compounds during hydrocarbon reforming process are poisons to reforming and shift catalysts used in fuel processor as well as electrode catalysts used in fuel cell stacks [4,5]. Consequently, the sulfur concentration in gasoline needs to be reduced to less than 1 ppmw for PEMFC and well below 10 ppmw for SOFC [5].

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Conventional processes and new approaches for desulfurization have been discussed in several recent reviews [1–3]. It is difficult to use the existing hydrotreating technology to reduce the sulfur content of liquid fuels to less than 10 ppmw, partly because the remaining sulfur compounds in current commercial gasoline and diesel fuels are thiophenic sulfur compounds which are relatively difficult to remove [1]. The technology requires an improved catalyst or increased reactor size and/or more severe operating conditions such as high H_2 pressure and high temperature to produce low-sulfur fuels. In the case of gasoline, the need to maintain the octane number by preserving the olefin during hydrodesulfurization makes it more difficult to reach ultra-deep sulfur removal to below 5 ppmw. Recently, the Conoco Phillips Petroleum company developed a new S-Zorb process for the production of low sulfur gasoline by reactive adsorption of sulfur compounds over a solid sorbent [6]. The process uses a fluidized-bed reactor in the temperature range between 377 and 502 °C under H_2 pressures in the range of 7.1–21.1 kg/cm². Similarly, the Research Triangle Institute (RTI) reported a TReND process for reactive desulfurization of gasoline over a metal oxide-sorbent at a temperature higher than 400 °C with a minimal hydrogen consumption [7]. On the other hand, the fuel cell applications require sulfur removal onboard or onsite at low temperatures without using H_2 gas. Consequently, development of a new process for deep desulfurization of liquid fuels under ambient conditions without using H_2 becomes one of the major challenges in fuel processing for the liquid hydrocarbon fuel-based fuel cell systems [1,3].

We recently proposed and have been exploring an approach at the Pennsylvania State University called selective adsorption for removing sulfur (PSU-SARS) over various materials under ambient conditions without using H_2 gas for fuel cell and refinery applications [1–3,8–15]. Various adsorbents including metals, metal halides, metal oxides, metal sulfides, and modified zeolites are being synthesized and evaluated in our laboratory [8–15]. The PSU-SARS approach [1,8,12] aims at removing sulfur compounds in gasoline and jet fuels selectively by a direct sulfur–adsorbent interaction, rather than π -complexation. Among several types of adsorbents explored, Ni-based adsorbents exhibited better performance for removing sulfur compounds (thiophene and benzothiophene) from a model gasoline containing about 400 ppmw sulfur together with 10 wt.% of aromatics [9]. The breakthrough adsorption capacity of the adsorbent was 12.3 mg S/g of the adsorbent (mg/g). The saturated adsorption capacity was 14.1 mg/g. The performance of these Ni-based adsorbents was evaluated in the desulfurization of real gasoline, diesel and jet fuels.

The desulfurization of transportation fuels over Cu(I)Y-zeolite via π -complexation under ambient conditions has been reported recently in several interesting publications by Yang and coworkers [18–20]. In the desulfurization of gasoline, the authors have reported that a breakthrough adsorption capacity of the Cu(I)Y-zeolite at the sulfur level of 0.28 ppmw was 0.14 mmol of sulfur per gram of adsorbent

(mmol/g) (corresponding to 4.5 mg S/g of adsorbent) and the saturated adsorption capacity was 0.39 mmol/g (corresponding to 12.5 mg S/g of adsorbent) [18]. In these studies, a gas chromatograph coupled with a flame photometric detector (GC-FPD) has been used for the quantitative analysis of total sulfur concentration in gasoline and diesel fuels obtained from adsorptive desulfurization [18–20].

For ultra-deep desulfurization, the accurate determination of sulfur content in the desulfurized fuels is extremely important in developing and evaluating new adsorbents and catalysts. On the other hand, analyzing and quantifying sulfur compounds at very low concentrations (e.g., 1–10 ppmw) is difficult, and the selection of proper methods requires careful consideration of multiple factors [21–31]. Several American Society for Testing and Materials (ASTM) methods such as Wavelength Dispersive X-ray Fluorescence Spectroscopy (Method D 2622), Ultraviolet Fluorescence method (Method D5453), Oxidative Microcoulometry method (Method D3120) have been specified for the determination of sulfur content in light hydrocarbons and petroleum products [16]. Gas chromatograph (GC) coupled with sulfur selective detectors such as flame photometric detector (FPD) or an improved FPD called pulsed flame photometric detector (PFPD) and GC coupled with atomic emission detector (AED) or sulfur chemiluminescence detection (SCD) have been used in several research laboratories for the quantitative estimation of sulfur compounds in commercial transportation fuels [17–20]. However, because of the special characteristics of the FPD and PFPD detectors, care must be taken while treating the GC-FPD/PFPD data. The use of the GC-FPD for the quantitative analysis would require consideration of the nonlinear response and quenching effects of FPD [21,22].

The main objective of this work was to examine and compare the performance of a supported Ni adsorbent and the Cu(I)Y-zeolite in the desulfurization of a commercial gasoline in fixed-bed adsorption experiments at room temperature and at 200 °C. Concordant with the goal of developing adsorbents towards ultra-deep desulfurization, we also examined the impact of analytical methods on sulfur quantification at lower ppm-level, which is critical for fuel cell applications. The analysis of desulfurized fuels was carried out using different methods including gas chromatographs coupled with flame ionization detector (GC-FID), flame photometric detector (GC-FPD) and pulsed flame photometric detector (GC-PFPD) and a total sulfur analyzer (TSA). The impact of analytical methods on the quantification of low sulfur liquid fuels has also been evaluated and reported here.

2. Experimental

2.1. Standard samples containing sulfur

In order to compare the accuracy of sulfur determination using different analytical methods, at least 10 standard

Table 1
Sulfur concentration of the standard fuel samples

No.	Sulfur concentration (ppmw S)				
	T	BT	DBT	4,6-DMDBT	Total S
1	127.0	117.0	107.0	109.0	460.0
2	63.5	58.5	53.5	54.5	230.0
3	31.8	29.3	26.8	27.3	115.0
4	12.7	11.7	10.7	10.9	46.0
5	6.4	5.9	5.4	5.5	23.0
6	3.2	2.9	2.7	2.7	11.5
7	1.3	1.2	1.1	1.1	4.6
8	0.64	0.59	0.54	0.55	2.30
9	0.32	0.29	0.27	0.27	1.15
10	0.13	0.12	0.11	0.11	0.46

samples containing known amounts of thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as sulfur compounds in *n*-decane with a total sulfur concentration ranging from 0.46 to 460 ppmw were prepared. All the sulfur compounds used for preparing standard samples were purchased from Aldrich and used as such without further purification. The sulfur concentrations (ppmw) of various

sulfur compounds present in the mixtures are summarized in Table 1.

2.2. Gasoline sample

A commercial gasoline sample was purchased from a local Exxon gasoline station in State College, Pennsylvania in July 2003. The total sulfur concentration in the gasoline was 305 ppmw according to our analysis using Antek 9000S total sulfur analyzer. The major sulfur compounds existing in the commercial gasoline of the present study are thiophene, 2-methylthiophene (2-MT), 3-methylthiophene (3-MT), 2,4-dimethylthiophene (2,4-DMT) and BT, as shown in Fig. 1. A model fuel containing 190 ppmw sulfur in the form of thiophene in *iso*-octane was also prepared for adsorptive desulfurization experiment.

2.3. Adsorbents

The nickel-based adsorbent used in the present study contained about 55 wt.% of Ni in metallic state with silica-alumina as a support and had a BET surface area of

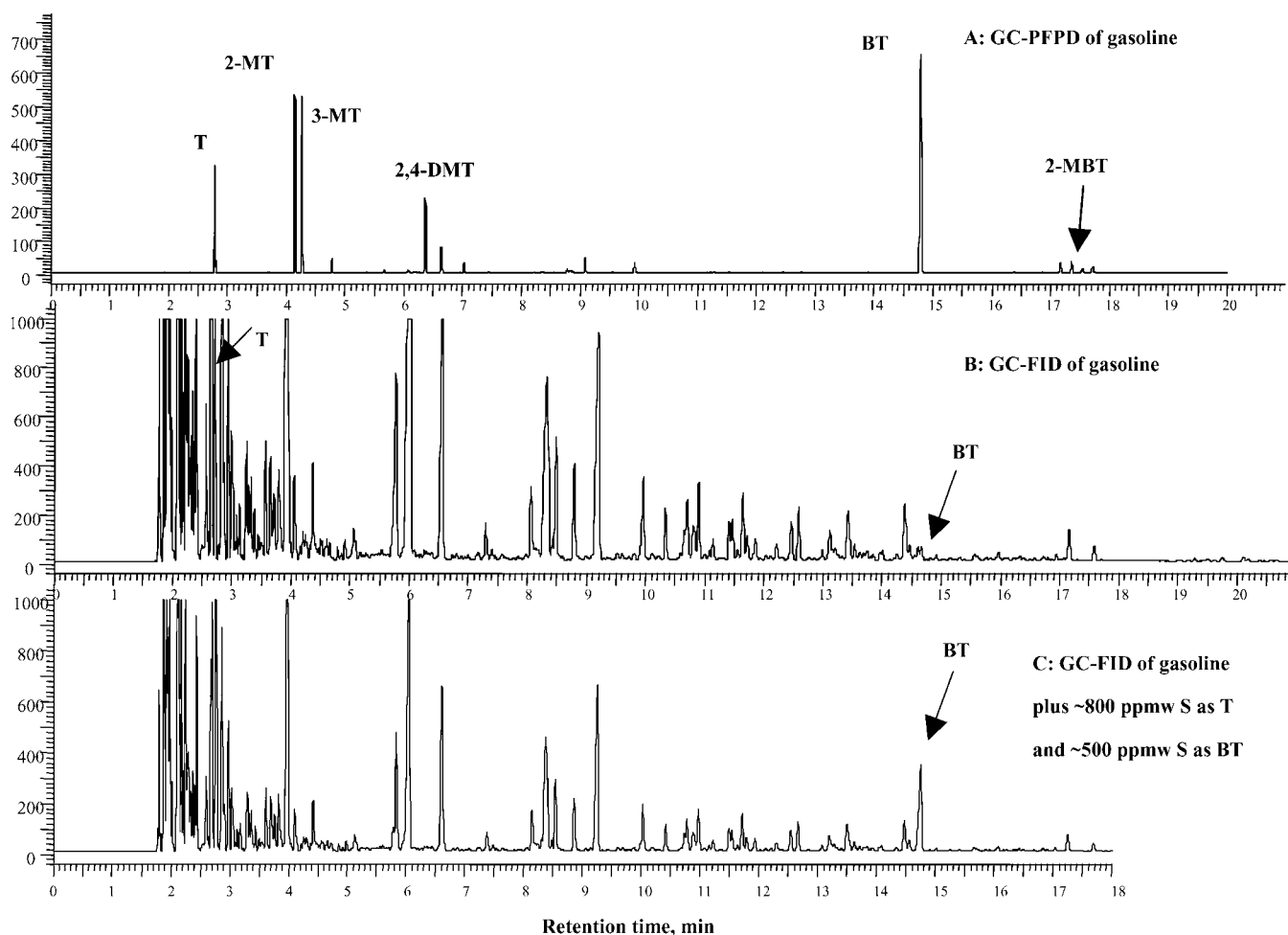


Fig. 1. GC-PFPD and GC-FID chromatograms of a commercial gasoline containing 305 ppmw sulfur, and GC-FID for the same gasoline with added thiophene (T, 800 ppmw S) and benzothiophene (BT, 500 ppmw S).

157 m²/g. The adsorbent in bulk (20–30 g) was pre-reduced in H₂ gas at 500 °C for 5–6 h, passivated using sulfur-free *n*-hexane and stored in the same solvent in an airtight sample bottle. The reduced Ni-based adsorbent is basically non-pyrophoric in the presence of *n*-hexane solvent and can be stored for several months without significant degradation in the activity of the sample. Cu(I)Y-zeolite was obtained by *in situ* He treatment of Cu(II)Y-zeolite, which in turn was obtained by ion-exchange of NaY-zeolite (Strem Chemicals) having a Si/Al ratio of 2.43 following the same preparation conditions as described in the literature [18–20].

Chemical composition of the parent NaY-zeolite as well as the Cu(II)Y-zeolite were determined by ICP elemental analysis using a high-resolution magnetic sector ICP-MS spectrometer (Finnigan; Element model-1). Samples were fused with lithium metaborate, dissolved in nitric acid and diluted as required. Cu, Si and Al were scanned in medium resolution against calibration standards. The instrumental detection limits for Si, Al and Cu were about 7 ppm, 400 ppt, and 50 ppt, respectively.

Temperature-programmed reduction (TPR) experiments on the Cu(II)Y-zeolite and Ni-based adsorbent were conducted on a Micromeritics 2910 TPD/TPR instrument. About 100 mg of the sample was loaded in the quartz reactor and reduced in 5% H₂/Ar mixture (50 cm³/min) at a heating rate of 5 °C/min up to 700 °C. The H₂ consumption due to the reduction of constituent metal ions was monitored simultaneously by TCD detector equipped with the instrument.

2.4. Fixed-bed adsorption experiments

Adsorption experiments were performed at room temperature and 200 °C under ambient pressure without using H₂ gas. About 3.0 g of the adsorbent was packed in a stainless steel column having a bed dimension of 4.6 mm i.d. and 150 mm length [8–15]. The packed column was placed in a multi-channel convection oven designed in our laboratory for the adsorption experiments. In order to ensure that the Ni in the Ni-based adsorbent is in the reduced form, the adsorbent bed was heated slowly (2 °C/min) up to 200 °C in H₂ gas (flow rate of 50–60 ml/min) at ambient pressure, and kept at 200 °C for 1 h in H₂ flow. The oven temperature was then decreased to the desired adsorption temperature (room temperature or 200 °C).

Adsorption experiments over Cu(I)Y-zeolite were similar to those reported in the literature [18–20]. The uncalcined Cu(II)Y-zeolite obtained by ion exchange was treated with He gas at 450 °C for 5–6 h and then the bed was cooled down to room temperature in He flow. The He gas used in the present study was dried by passing the gas through a trap packed with 3A type zeolite. The bed was tapped to ensure proper packing and then a sulfur-free *n*-decane was passed through the adsorbent bed for about 10 min by means of an HPLC pump at a flow rate of 0.2 or 0.5 ml/min. The feed was then switched to the commercial gasoline with the same flow rate as that of *n*-decane. After making sure that the

sulfur-free *n*-decane in the adsorbent bed and in the line was replaced by the commercial fuel, the effluent from the adsorbent bed was collected periodically every 10–20 min and analyzed using GC-FPD/GC-PFPD and Antek 9000S total sulfur analyzer.

2.5. GC-FPD analysis

A SRI 8610C gas chromatograph with a capillary column, XTI-5 (Restek, bonded 5%, 30 m × 0.50 mm i.d. × 0.50 μm film thickness), a flame photometric detector (FPD), and an on-column injector was used for GC-FPD analysis. Ultra-high purity helium was used as carrier gas. The column temperature was programmed, 120 °C for 2 min, 6 °C/min from 120 to 170 °C, 20 °C/min from 170 to 290 °C, hold for 2 min. The injection volume of sample was 2.5 μl.

2.6. GC-PFPD/FID analysis

A Hewlett-Packard 5890 series II gas chromatograph with a capillary column, XTI-5 (Restek, bonded 5%, 30 m × 0.25 mm i.d. × 0.25 μm film thickness) and a split mode injector (ratio 100:1) was used with ultra-high purity helium as a carrier gas. The injector temperature was kept at 290 °C. A pulsed flame photometric detector (PFPD, O.I. Analytical 5380) and a flame ionization detector (FID) were used for GC-PFPD and GC-FID analysis, respectively. For analysis of the standard samples, the column temperature program was the same as that used for GC-FPD analysis and the injection volume was 3 μl. For the real gasoline and treated gasoline samples, the column temperature was set at 50 °C for 2 min, 6 °C/min from 50 to 152 °C and the injection volume was 2 μl.

2.7. Total sulfur analysis

The total sulfur concentrations in the standard samples, commercial gasoline and desulfurized gasoline were determined using an Antek 9000S total sulfur analyzer. The instrument was calibrated in our laboratory at four different sulfur concentration ranges: 0–6, 6–60, 60–300 and 300–900 ppmw sulfur using dibenzothiophene (DBT) in *n*-decane as a solvent and linear calibration curves were obtained for each calibration range. The linearity of the calibration in each range was also cross-checked using sulfur standard samples supplied by Antek. The sulfur detection limit of the total sulfur analyzer in the normal working range is 0.5 ppmw sulfur.

3. Results and discussion

3.1. Analysis of standard samples using GC-FPD, GC-PFPD and total sulfur analyzer

Fig. 1 shows the GC-PFPD and GC-FID chromatograms of the gasoline, which illustrates the complexity of the real

fuel samples and the overlapping of hydrocarbons with sulfur compounds. Since the species that is being measured in FPD is electronically excited diatomic sulfur, the response of the FPD for sulfur compounds is inherently nonlinear [21,22]. It has been found that the intensity of the sulfur emission in FPD is given by Eq. (1) [23–27]

$$I \propto [S]^n \quad (1)$$

where I is the intensity of the sulfur emission, $[S]$ is the sulfur concentration in the sample. The exponent “ n ” is referred to as the exponential proportionality constant.

The intensity of the sulfur signal is theoretically proportional to the square of the sulfur concentration in the flame, i.e. the value of “ n ” is close to 2 [21,22,26]. In practice, the “ n ” value depends on the operating conditions of the FPD and also depends on the nature of the sulfur compound. In order to determine the “ n ” value experimentally, Eq. (1) can be modified as:

$$A_i = f_i [S_i]^n \quad (2)$$

or

$$\ln A_i = n \ln [S_i] + \ln f_i \quad (3)$$

where $[S_i]$ and A_i are the sulfur concentration and the corresponding peak area of sulfur species “ i ”, respectively; f_i is a correction factor for the sulfur species “ i ”. As indicated by Farwell and Barinaga [23] for a series of sulfur compounds, the regression between A and $[S]$ gave “ n ” values in the range 1.75–2.25 with R^2 values of 0.99. A study by Zoccolillo et al. [28] showed that the “ n ” value for six sulfur compounds, including benzothiophene, is similar, being 1.978 with a R^2 value of 0.995.

For determining the total sulfur concentration of the sample containing more than one sulfur compound, Eq. (3) could be modified as:

$$[S]_t = \sum [S_i] = \sum g_i A_i^{1/n} \quad (4)$$

where $[S]_t$ is the total sulfur concentration in the sample, and $g_i = f_i^{-1/n}$. For many sulfur compounds, g_i value is similar, and thus, Eq. (4) can be written as:

$$[S]_t = \sum [S_i] = g \sum A_i^{1/n} \quad (5)$$

It should be pointed out that the sum of the areas of the all peaks obtained normally by the GC-FPD/PFPD integrator in the analytical report should not be used for determining the total sulfur concentration, because $\sum A_i^{1/n} \neq (\sum A_i)^{1/n}$ [28]. Thus, it is necessary to determine the sulfur concentration corresponding to each peak, and then to sum the concentrations for each sulfur compounds.

In addition to the nonlinearity of the response, another factor that one has to take into account in determining sulfur concentration of hydrocarbon fuels using GC-FPD method is the quenching effect, which arises due to the co-elution of hydrocarbons along with sulfur compounds [21,22]. The quenching effect is very severe in determining the total

sulfur content in commercial transportation fuels as they contain over hundreds of different hydrocarbons compounds, and the concentrations of numerous hydrocarbon components are several orders of magnitude higher than those of individual sulfur compounds in the fuels, as can be seen from Fig. 1. Co-elution of these compounds along with sulfur compounds in the GC-FPD analysis significantly suppresses the response produced by the sulfur compounds. This reduction in FPD response is attributed to non-radiative collisional quenching on S_2^* in the flame by CO_2 , CH_4 , and other combustion products from the co-eluted hydrocarbons [21,22]. Zoccolillo et al. [28] reported that the FPD response for sulfur compounds in a diesel fuel was reduced due to the quenching effect by a factor in the range between 0.16 and 1.0, depending on the amount of the hydrocarbon co-eluted.

The quantitative analysis of the standard samples by GC-FPD was conducted. We observed that the response-concentration has an exponential characteristic. An excellent linear relationship between $\ln A_i$ and $\ln [S_i]$ could be obtained with a R^2 value higher than 0.99 when the sulfur concentration for each sulfur compound is less than 32 ppmw. However, the $\ln A$ versus $\ln [S_i]$ curve turned down, when the sulfur concentration was higher than 32 ppmw, probably due to self-quenching or self-absorption [22]. When the sulfur concentration for each sulfur compound was less than 1 ppmw, no peak corresponding to sulfur could be detected under the present GC-FPD operating conditions. The regression analysis of our GC-FPD data shows that the “ n ” values (slope) are similar for all the four sulfur compounds, and they are 2.05, 2.08, 2.02 and 2.01 for T, BT, DBT and 4,6-DMDBT, respectively.

Relative to FPD, better analytical results can be obtained using PFPD in general as the flame chemiluminescence light emission is pulsed and its peak intensity is largely increased [29]. The detector operates with a fuel-rich mixture of hydrogen and air. This mixture is ignited and then propagated into a combustion chamber three to four times per second where the flame front extinguishes. Carbon light emission and the emissions from the hydrogen/oxygen combustion flame are complete in 2–3 ms, after which a number of heteroatomic species give delayed emissions which can last for 4–20 ms. These delayed emissions are filtered with a wide band pass filter, detected by a photomultiplier tube, and electronically gated to eliminate background carbon emission (self-quenching). The PFPD is characterized by the additional dimension of a light emission time and the ability to separate in time the emission of carbon species from that of sulfur, resulting in a considerable enhancement in the detection selectivity [30,31]. In addition, the detection sensitivity is improved and the self-quenching is reduced through the ability to inject smaller samples.

The quantitative analysis of the standard samples by GC-PFPD was also conducted. Similar to that observed in the GC-FPD analysis, the $\ln A_i$ and $\ln [S_i]$ exhibited a good linear relationship for the sulfur concentration less than 32 ppmw for each sulfur compounds. When the sulfur concentration is

higher than 32 ppmw, the corresponding GC-PFPD chromatogram shows an inverted-W shaped peak, indicating that the sulfur concentration in the sample exceeds the normal working range of the PFPD detector and the corresponding data cannot be used. When the sulfur concentration for each sulfur compound in the samples is less than 0.5 ppmw, no peak was observed under the same instrumental conditions. The regression analysis of our GC-PFPD data shows that the “ n ” value (slope) is also similar for the four sulfur compounds and they are 1.74, 1.90, 1.93 and 1.97 for T, BT, DBT and 4,6-DMDBT, respectively. The “ n ” values from our GC-FPD and GC-PFPD analysis are close to the theoretical and experimental values reported in the literature [21,22,28]. The data for the quantitative analysis using GC-FPD/PFPD will be discussed separately.

3.2. Comparison of different analysis methods

For comparison, the standard fuel samples have also been analyzed using a total sulfur analyzer. Unlike that in FPD or PFPD, the sulfur-containing sample in the total sulfur analyzer (TSA) is oxidized in a furnace at 1050 °C using an oxygen-rich atmosphere. The resulting SO₂ is then irradiated by ultraviolet excitation source. The excited SO₂ then relaxes, emitting light that passes through an optical filter. This emission is recorded. It has been reported that the Antek 9000S analysis method complies with the ASTM Ultraviolet Fluorescence method (Method D5453) specified for the determination of total sulfur content in liquid hydrocarbon fuels, and oils [32]. Fig. 2 presents a plot of measured sulfur concentrations versus the expected sulfur concentrations based on the amount of sulfur compounds. It is clear that the measured sulfur content by TSA coincides very well with the expected sulfur content in the entire concentration range. The accuracy of the measured sulfur concentration is satisfactory.

The impact of method of analysis on the accuracy in determining the total sulfur content in the standard samples has also been examined in this work. The data obtained from GC-FPD and GC-PFPD have been treated both as a linear response as well as an exponential response. In treating the data as a linear response, the total sulfur concentration ($[S]_t$) can be written as shown in Eq. (6):

$$[S]_t = \sum [S_i] = \sum g_i A_i \quad (6)$$

If the g_i is assumed to be the same for all the standard sulfur compounds used in the present study, then Eq. (6) will become

$$[S]_t = g_i \sum A_i = g A_t \quad \text{or} \quad \frac{[S]_t}{[S_0]} = \frac{A_t}{A_0} \quad (7)$$

where A_t and A_0 are the total area under all peaks for the sample under investigation and that for a known sample (such as initial feed), respectively. $[S_0]$ is the sulfur concentration in the known sample. Using a known sample having a sulfur

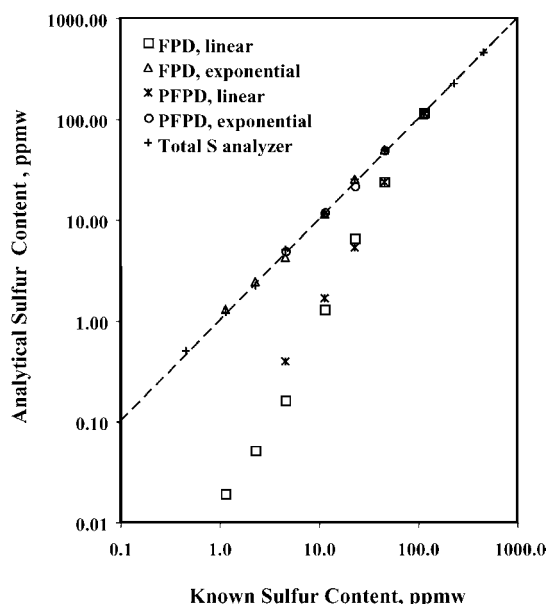


Fig. 2. Comparison of different analytical methods for the determination of total sulfur contents in the standard fuel samples.

content $[S_0] = 115$ ppmw, the $[S]_t$ values calculated by using Eq. (7) for data obtained from GC-FPD and GC-PFPD are shown in Fig. 2. Clearly, the sulfur contents estimated using linear treatments of the data obtained from GC-FPD and GC-PFPD deviate and yield significantly lower values than that theoretically anticipated, particularly in the lower sulfur levels. For instance, for a standard sample having a sulfur concentration around 1 ppmw, the estimated sulfur content using GC-FPD and GC-PFPD by the linear treatment is only around 0.02 ppmw. The error will further increase with the increase in $[S_0]$ value and with the decrease in the actual sulfur concentration of the sample.

On the other hand, the error in determining the sulfur content using GC-FPD and GC-PFPD could be minimized by treating the data as exponential response. The total sulfur concentration in a fuel using exponential response of GC-FPD and GC-PFPD can be calculated by using Eq. (4). Since only n -decane has been used as a solvent in the standard samples and its retention time is significantly different from those sulfur compounds used as standards, here we assume that the quenching effect due to co-elution of n -decane is negligible. The $[S]_t$ values calculated using Eq. (4) for the data obtained from GC-FPD and GC-PFPD is also included in Fig. 2 itself. As can be seen, these data points nicely coincide with those obtained from total sulfur analyzer, indicating that the GC-FPD or GC-PFPD analysis methods can yield satisfactory results in the working range of the detector for the standard samples if the data are treated as an exponential response rather than as a linear response.

3.3. Characterization of the adsorbents

Table 2 compares the chemical composition of the Cu(II)Y-zeolite used in the present study with that of the

Table 2
Chemical composition of zeolite adsorbent

Adsorbent	Cu/Al molar ratio	Si/Al molar ratio
NaY-zeolite	–	2.75
Cu(II)Y-zeolite	0.35	3.09

parent NaY-zeolite. There is a small increase in the Si/Al molar ratio from about 2.8 for the parent NaY-zeolite to about 3.1 for the Cu(II)Y-zeolite. The Cu/Al ratio in the Cu(II)Y-zeolite is about 0.35. If we assume that each Cu^{2+} ion can compensate two aluminum tetrahedra in the zeolite framework, then the extent of ion exchange in our case is about 70%, i.e. $2\text{Cu}/\text{Al} = 0.70$. The Cu/Al ratio of Cu(II)Y-zeolite (0.35) used in the present study is very close to that (0.36) reported in the literature for the adsorptive desulfurization of transportation fuels by π -complexation [33].

The temperature programmed reduction (TPR) profiles of the Ni-based adsorbent and Cu(II)Y-zeolite are shown in Fig. 3. The Ni-based adsorbent shows a maximum rate of H_2 consumption around 248 °C probably due to the reduction of surface nickel oxide layer since the adsorbent is pre-reduced and stored in hexane solvent and dried before using for TPR and adsorbent experiments. H_2 consumption also occurs above 500 °C, which is likely due to the reduction of supported Ni^{2+} ions. The Cu(II)Y-zeolite, dried around 200 °C exhibits an intense peak around 215 °C together with a small shoulder around 290 °C. Earlier study on the TPR of various zeolites exchanged with Cu(II) ion indicates that reduction occurs one or two stages depending upon the type of zeolite and the Si/Al ratio [34]. In most cases, the main reduction peak occurred between 150 and 300 °C and the peak has been attributed to the reduction of Cu^{2+} to Cu^0 and/or Cu^{2+} to Cu^+ as these reductions occur in the same

temperature range [34]. The subsequent reduction of Cu^+ to Cu^0 has been observed at relatively higher temperatures, around 600 °C. The main reduction peak around 215 °C in the Cu(II)Y-zeolite of the present study could be attributed to the reduction of Cu^{2+} ion-exchanged in the zeolite matrix to Cu^0 . No other reduction peak attributed to the reduction of Cu^+ to Cu^0 has been observed until 600 °C.

3.4. Adsorptive desulfurization of gasoline

Various new adsorbents, including zeolites, supported metals and other porous materials are being studied in our laboratory for the desulfurization of gasoline, diesel and jet fuel for fuel cell applications. The sulfur compounds over these adsorbents are selectively removed mainly by a direct sulfur–adsorbent/metal interactions [8–15] and this is in contrast to the π -complexation method reported very recently [18–20,33,35]. While the π -complexation concept is very interesting, it is not clear how the π -complexation adsorbents can effectively distinguish the ppmw levels of thiophenic sulfur compounds from 15–20 wt.% of aromatics and olefins present in gasoline. It should be noted that the heats of adsorption for thiophene (21–22 kcal/mol) and benzene (20–22 kcal/mol) are very close to each other over Cu(I)Y- and AgY-zeolites according to the estimation by Takahashi et al. [35] and the π -electron density on olefins is much higher than that on thiophenic sulfur compounds. The aromatics and olefins can strongly compete with thiophenic sulfur compounds on surface by π -complexation. Our recent studies on the adsorptive removal of thiophene from *iso*-octane over Ag-exchanged Y-zeolite indicated that the sulfur adsorption capacity decreased by about 18 times when 10 wt.% of toluene (aromatic) was added to the fuel. Similarly, the addition of 10 wt.% of 1-octene (olefin) decreased the adsorption performance by six times [13]. These results revealed that the aromatics present in the fuel strongly compete with sulfur in the adsorptive removal of sulfur compounds. Consequently, new adsorbents that can selectively remove sulfur compounds by direct sulfur–adsorbent/metal interactions are being developed in our laboratory [8–15] for the adsorptive desulfurization of gasoline and jet fuels.

In order to compare the performance of the Ni-based adsorbent being studied in our laboratory with that of the Cu(I)Y-zeolite, the best adsorbent reported in the literature [18–20], the later adsorbent has been synthesized using the same procedure as reported [19,35]. However, the specific dimension of the adsorption bed used for the desulfurization of gasoline and diesel as well as LHSV (liquid hourly space velocity) is not available in the literature [18–20,33,35]. It has been observed from our ongoing research that the adsorption bed dimensions (aspect ratios) and LHSV play a crucial role in the adsorption capacity [36]. Better performance has been observed using a longer bed and narrow internal diameter (i.d.). We first performed the tests for removing thiophene from *iso*-octane using bed dimen-

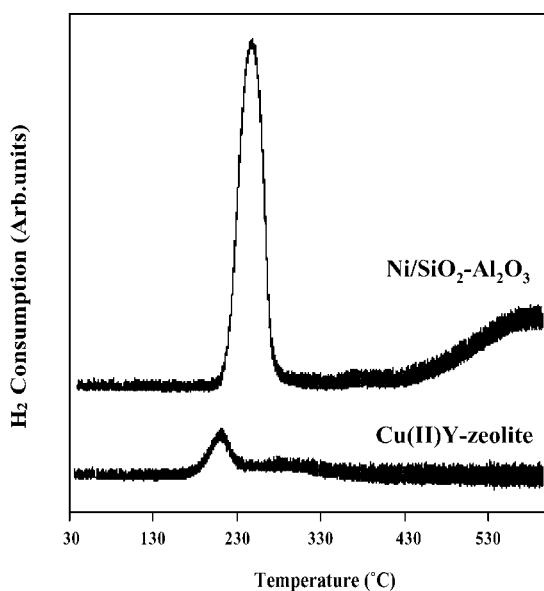


Fig. 3. Temperature-programmed reduction profiles of Ni/SiO₂–Al₂O₃ and Cu(II)Y-zeolite adsorbents.

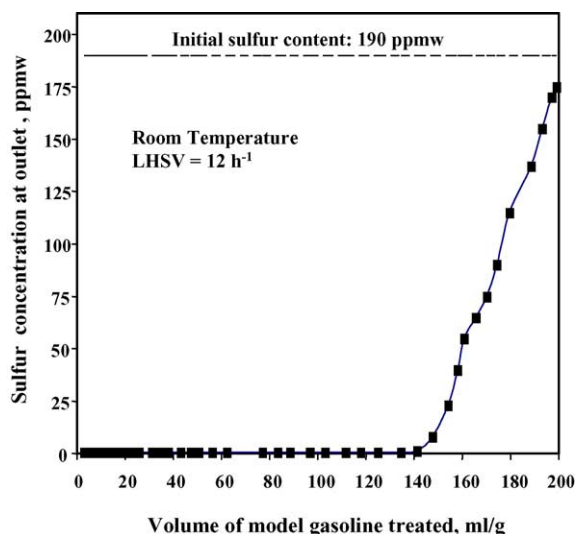


Fig. 4. Breakthrough curve for the adsorptive removal of thiophene over Cu(I)Y-zeolite at room temperature. The experimental conditions are very similar to those reported in the literature [35].

sions of 4.6 mm i.d. and 150 mm length. The initial sulfur content in the fuel was 190 ppmw sulfur (500 ppmw thiophene), which is the same as that described in a recent literature [35].

Fig. 4 shows the breakthrough curve for the adsorptive removal of thiophene from *iso*-octane over Cu(I)Y-zeolite synthesized in our laboratory. Under the present experimental conditions, about 134 ml of the fuel has been desulfurized to below 1 ppmw sulfur (0.5 ppmw is the detection limit of the Antek total sulfur analyzer) using 1 g of the Cu(I)Y-zeolite, corresponding to a breakthrough capacity of 17.8 mg S/g of the adsorbent (mg/g). This capacity is similar to that reported recently (about 125 ml of the fuel/g of Cu(I)Y-zeolite, corresponding to a breakthrough capacity: 16.6 mg/g) [35]. We then tested the same batch of the Cu(I)Y-zeolite in the desulfurization of a commercial gasoline containing 305 ppmw sulfur using the same experimental conditions, but the desulfurized fuel was analyzed using the total sulfur analyzer rather than a GC-FPD.

Fig. 5 shows the breakthrough curves for the adsorptive desulfurization of the commercial gasoline over Cu(I)Y-zeolite performed using 0.5 ml/min (liquid hourly space velocity, LHSV = 12 h⁻¹) and 0.2 ml/min (LHSV = 4.8 h⁻¹). Although the material exhibited performance very close to that reported [33] for removing thiophene from *iso*-octane (Fig. 4), the very first fraction collected from gasoline desulfurization contained above 150 ppmw sulfur at the flow rate of 0.5 ml/min for the commercial gasoline (Fig. 5). The sulfur content in the treated fuel reached the initial concentration within 30 min. Desulfurization to below 1 ppmw S could only be noticed in the first fraction when the flow rate of the fuel was decreased to 0.2 ml/min (LHSV = 4.8 h⁻¹). Under these experimental conditions, about 1 ml of the commercial gasoline has been desulfurized using 1 g of the Cu(I)Y-zeolite with an outlet sulfur content of below

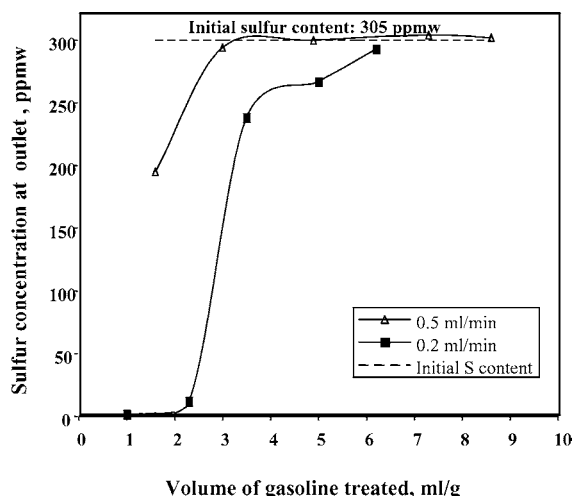


Fig. 5. Breakthrough curves for the adsorptive desulfurization of commercial gasoline (305 ppmw S) over Cu(I)Y-zeolite. The desulfurized fuels were analyzed using total sulfur analyzer rather than GC-FPD. The adsorbent preparation and testing conditions are similar to those reported in the literature [18,19,35].

1 ppmw, corresponding to an adsorption capacity of 0.22 mg/g of adsorbent. The breakthrough capacity of the Cu(I)Y-zeolite at an outlet sulfur level of 10 ppmw is about 0.49 mg/g. Relative to the case with model fuel, the much lower capacity of Cu(I)Y-zeolite for the desulfurization of the commercial gasoline clearly indicates that other components in the real gasoline such as the aromatics and olefins might strongly compete with the adsorption of thiophenic sulfur compounds by π -complexation.

On the other hand, we have found that temperature can have a significant effect on adsorption desulfurization of liquid fuels. We have been working on the development of new adsorbents for the adsorptive removal of sulfur compounds present in logistic fuels (jet fuel and diesel fuel) at different temperatures and at various adsorption bed dimensions. A Ni-based adsorbent exhibited a high adsorption capacity over 11 mg/g around 220 °C for a jet fuel sample (containing 380 ppmw S) at the outlet sulfur content below 30 ppmw, without developing any significant pressure drop (<2 psi) across the bed [36]. This adsorbent was tested for the adsorptive desulfurization of the commercial gasoline having 305 ppmw sulfur at room temperature (27 °C) and at 200 °C using a LHSV of 4.8 h⁻¹.

Fig. 6 shows the results of gasoline desulfurization using the Ni-based adsorbent at room temperature and 200 °C. At room temperature, the sulfur concentration determined by the total sulfur analyzer exceeds 1 ppmw when the effluent volume reaches 1.7 ml of the treated gasoline per gram of adsorbent (ml/g), meaning that under the present experimental conditions, 1 g of the adsorbent cleaned about 1.7 ml of commercial gasoline containing 305 ppmw of sulfur to below 1 ppmw. The corresponding adsorptive capacity is 0.37 mg/g. This capacity is about 1.7 times higher than that observed over Cu(I)Y-zeolite (0.22 mg/g) under the same experimental conditions.

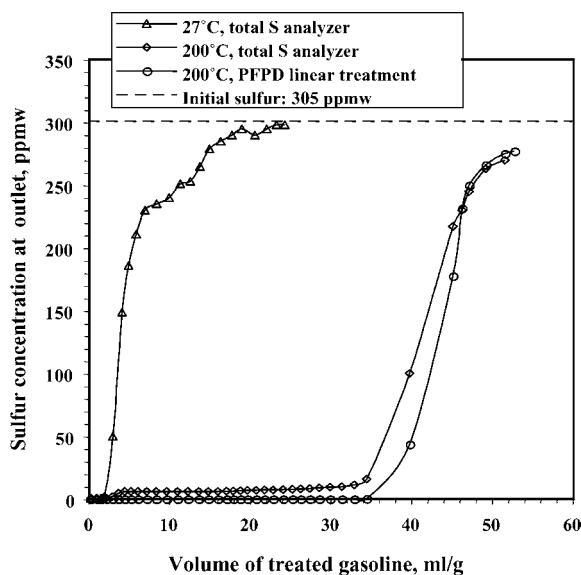


Fig. 6. Breakthrough curves for the adsorptive desulfurization of commercial gasoline over Ni-based adsorbent. The sulfur analysis data were obtained from both total sulfur analyzer and GC-PFPD.

The increase in temperature of adsorption has a major impact on the breakthrough capacity and saturation capacity of the Ni-based adsorbent. The breakthrough capacity increases by 38% when the adsorption is performed at 200 °C, being 0.51 mg/g at the outlet sulfur level of 1 ppmw. Unlike that observed at room temperature, the outlet sulfur content at 200 °C increased very slowly. The results indicate that at 200 °C, a gram of the material is capable of cleaning about 32 ml of the commercial gasoline to below 10 ppmw. The corresponding adsorption capacity at this sulfur level is about 7.3 mg/g and the saturation capacity is about 10 mg/g, which is much better than that of the Cu(I)Y-zeolite.

Table 3 shows the impact of using different analytical methods on the reported values of adsorption desulfurization performance for the Ni-based adsorbent at 200 °C. The total sulfur analysis and the GC-PFPD analysis have been conducted on all the desulfurized gasoline samples. In Table 3, the data from total sulfur analysis are compared to those from GC-PFPD using the linear response of the FPD using Eq. (7) without considering the quenching effect. The data correspond to Fig. 6. As can be seen, the breakthrough curve based on the data obtained from GC-PFPD lies on the X-axis (0 ppmw S) until the cumulative effluent volume reaches 34.1 ml/g of adsorbent (fraction #32). However, for the same samples, the data obtained using the total sulfur analyzer for all the fractions beyond elution volume of 2 ml lies above 1 ppmw S, well above that of the GC-PFPD data points, indicating that significant amount of sulfur is present in these samples. In fact, the total sulfur analyzer results showed that the sulfur content in the fraction #32 was 16 ppmw although the GC-PFPD gave only 0.4 ppmw sulfur. Thus, based on the GC-PFPD data alone, it could be stated that 1 g of the Ni-based adsorbent produced about 34.1 ml of “sulfur-free”

Table 3

Comparison of sulfur contents by total sulfur analysis and by GC-PFPD using linear response method for the gasoline samples desulfurized over Ni-based adsorbent at 200 °C

Fraction number	Treated volume (ml)	Total sulfur analyzer S (ppmw)	GC-PFPD linear response S (ppmw)
0	0.4	<0.5	0.0
1	1.1	<0.5	0.0
2	1.6	<0.5	0.0
3	2.3	1.0	0.0
4	3.0	2.0	0.0
5	3.7	4.5	0.0
6	4.5	6.0	0.0
7	5.3	6.0	0.0
8	6.1	6.0	0.0
9	7.2	6.0	0.0
10	8.3	6.0	0.0
11	9.6	6.0	0.0
12	11.0	6.0	0.0
13	12.2	6.0	0.0
14	13.6	6.1	0.0
15	14.7	6.1	0.0
16	15.9	6.2	0.0
17	17.0	6.3	0.0
18	17.8	6.4	0.0
19	18.6	6.8	0.0
20	19.5	7.0	0.0
21	20.6	7.1	0.0
22	21.6	7.3	0.0
23	22.7	7.4	0.0
24	23.9	7.5	0.0
25	25.1	7.9	0.0
26	26.1	8.2	0.0
27	27.2	8.5	0.0
28	28.3	9.0	0.0
29	29.7	9.5	0.0
30	31.1	10.0	0.0
31	32.6	11.2	0.0
32	34.1	16.0	0.4
33	39.4	100.0	43.4
34	44.7	217.0	177.6
35	45.8	230.0	231.7
36	46.7	245.0	250.0
37	48.7	263.0	266.0
38	51.1	270.0	275.0
39	52.3	273.0	277.1

gasoline and had a breakthrough capacity of 7.5 mg/g. However, most of the desulfurized fuel fractions are not truly “sulfur-free”, but contained up to 16 ppmw sulfur.

Fig. 7 shows the GC-PFPD chromatograms of some of the gasoline samples desulfurized with the Ni-based adsorbent at 200 °C together with corresponding sulfur concentrations determined using total sulfur analyzer. As can be seen, the GC-PFPD did not show any peak for sulfur compounds until the fraction #32 under the analytical conditions employed. It should be noted that higher injection volume is not good for determining the sulfur content as the quenching effect will be more severe due to the co-elution of larger amount of hydrocarbons. The sulfur concentration corresponding to each sulfur compound in the treated gasoline is only in ppmw-level, compared to the co-eluted hydrocarbons which are higher by orders of magnitudes.

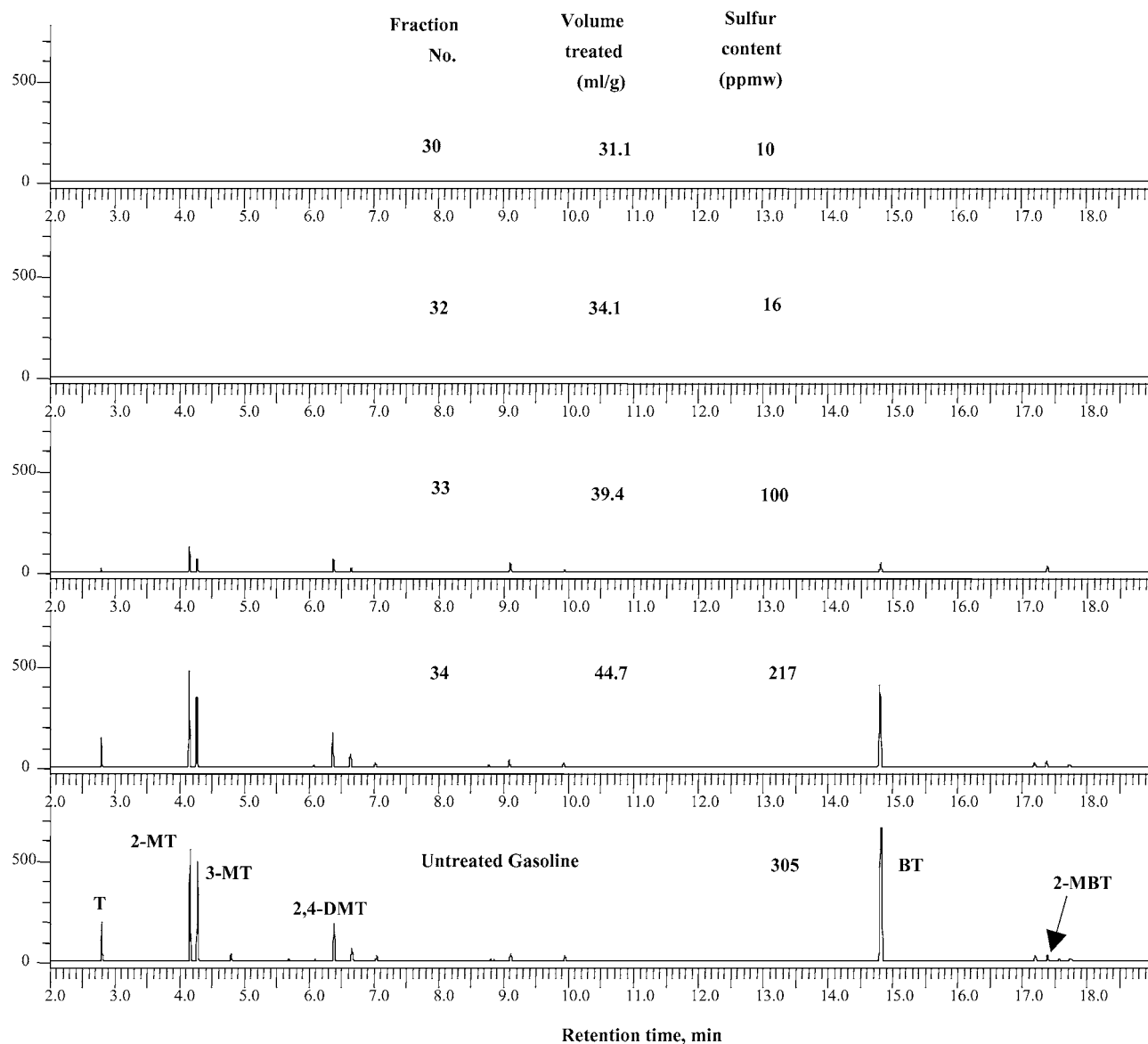


Fig. 7. GC-PFPD chromatogram of commercial gasoline and desulfurized gasoline over Ni-based adsorbent at 200 °C. The fraction number and sulfur content correspond to those in Table 3.

No GC-PFPD peaks were observed for the desulfurized gasoline sample (fraction #30) that still contained 10 ppmw S as revealed by the total sulfur analyzer, although we were able to detect 0.5 ppmw sulfur for each sulfur compound in the standard sample using *n*-decane as a solvent under the same GC-PFPD operating conditions. This indicates that the quenching effect due to the co-eluted hydrocarbons contributes significantly; thus GC-FPD or GC-PFPD method might underestimate the sulfur compounds in the desulfurized commercial transportation fuels. As can be seen from Fig. 1, the co-elution of hydrocarbons with sulfur compounds is significant in the GC analysis of the commercial transportation fuels and this would severely interfere with the quantitative analysis using FPD or PFPD detectors.

It is therefore clear that the analysis of the total sulfur concentration in real fuels by using GC-FPD or GC-PFPD without considering both the nonlinear response and the quenching effect can lead to erroneous results, particularly for low-sulfur fuels from desulfurization over solid adsorbents. A total sulfur analyzer with careful calibration is expected to provide more reliable results, especially in the low ppm-levels of sulfur concentrations.

4. Conclusions

The use of selective adsorbents can achieve ultra-deep desulfurization of commercial gasoline to below 1 ppmw or below 10 ppmw sulfur, depending on the needed level of

sulfur removal, the type of fuel cells and the requirements for adsorbent capacity. Both the type of adsorbents and the conditions of adsorption play an important role.

The Cu(I)Y-zeolite prepared in the present study showed a breakthrough capacity of 0.22 mg/g at room temperature for removing sulfur from a commercial gasoline to <1 ppmw. Under the same experimental conditions, a Ni-based adsorbent exhibited a breakthrough capacity of 0.37 mg/g for the commercial gasoline desulfurization (to <1 ppmw S).

Increasing the adsorption temperature from room temperature to 200 °C further raised the breakthrough capacity of the Ni-based adsorbent by 38%. The adsorptive capacity of the Ni-based adsorbent corresponding to the outlet sulfur level of 10 ppmw is 7.3 mg/g, which is much better than that of the Cu(I)Y-zeolite (0.49 mg/g).

Analysis of a series of the standard fuel samples and real gasoline samples by GC-FPD, GC-PFPD and total sulfur analyzer indicated that: (1) In the normal working range of the FPD and PFPD detectors, the response is not linear but exponential. The value of the exponent “*n*” being around 2, in agreement with literature reports [23,28]. (2) The quenching effect is significant in the analysis of the real gasoline samples by GC-FPD and GC-PFPD due to the co-elution of hydrocarbons along with sulfur compounds present in the fuel.

Consequently, when the total sulfur contents are in the low ppmw range (e.g., <10 ppmw), the existing GC-FPD and the GC-PFPD methods are not suitable for quantitative analysis of total sulfur concentration in complex hydrocarbon matrices (such as commercial gasoline, diesel and jet fuels) without considering both the nonlinear response and the quenching effect.

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